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USE OF RARE-EARTH METAL OXIDES FOR DECORATION OF PORCELAIN

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A variant of use of rare-earth metal oxides for decoration of porcelain is examined. The effect of these oxides on phase formation and on the character of coloring of the structure on incorporation in the paste is examined.

Underglaze painting is widely used as a type of decoration in many porcelain factories in the country. The palette of different underglaze colors is greatly limited by the fact that the coloring pigments can burn off or be reduced at high temperatures (1300 – 1420°C) and in the reducing character of the gas medium [1, 2]. For this reason, it becomes necessary to use high-temperature coloring compounds which are stable in these conditions. Rare-earth metal oxides (REMO) are such compounds. They can be used as components of paints for decorating porcelain articles and as a constituent part of the mass which has the property of coloring porcelain. Some properties and the color range of a series of REMO are reported in Table 1 [3].

Coloring porcelain paste allows manufacturing porcelain for different applications: artistic, household, industrial, etc. One of the main problems in coloring the paste is giving the porcelain previously known coloristic and esthetic characteristics while preserving all of the properties of classic porcelain.

The optimum amount of REMO (5.0 – 7.5%) [4] was added to porcelain paste of the following composition (mass content, %): 66.21 SiO_2, 21.12 Al_2O_3, 0.29 Fe_2O_3, 0.69 CaO, 0.47 MgO, 1.83 K_2O, 0.85 Na_2O, 0.13 TiO_2, 6.31 calcination loss.

The porcelain samples underwent microscopic analysis [5, 6]. Petrographic analysis showed (Table 2) that incorporation of REMO in the porcelain changed its structure. With respect to the character of the effect of the REMO on coloration of the porcelain samples, they can be divided into two groups:

forming crystal aggregates in the structure of the porcelain (Er_2O_3, CeO_2);

not forming a crystalline phase but forming colored glass (Nd_2O_3, Pr_6O_{11}).

The boundaries of the pseudomorphoses with respect to feldspar are basically preserved and the size of the mullite needle network is 2 – 10 μm, less frequently up to 15 – 20 μm, the mullite in the basic paste is less than 1 μm in size, and aggregates are pronounced.

All of the REMO alter the porosity and increase the amount of glass phase, manifested by perfection of the shape of the pores and slight improvement in the character of mullitization. Their effect is especially marked in blue porcelain containing Nd_2O_3 (with respect to the structure, this is a porcelain of a normal degree of ripeness but with slightly larger pores).

A possible cause of the appearance of isolated pores and sections of glass in incorporation of REMO is inadequate dispersion of the pigment in the paste, which can be eliminated by combined disaggregation of the components of the porcelain paste.

X-ray phase analysis of the porcelain samples with REMO showed that CeO_2 forms an eutectic with mullite while Nd_2O_3 and Er_2O_3 forms the chemical compounds $2Nd_2O_3 \cdot 3SiO_2$ and $Er_2O_3 \cdot 2SiO_2$. An insignificant decrease in mechanical strength (by approximately 4.3%) is observed

TABLE 1

Oxide	Density, g/cm³	Melting point, °C	$-\Delta H^0_{298(f)}$, kJ/mole	$-\Delta G^0_{298(f)}$, kJ/mole	Color	
					oxide	porcelain after addition of oxide
Nd_2O_3	6.59	2320	1808.3	1721.3	Light blue	Blue
Ho_2O_3	8.41	2360	1881.1	1791.6	Yellow	Dark yellow
Er_2O_3	8.66	2380	1987.9	1808.7	Pink	
CeO_2	7.22	2600	1087.6	1024.5	Light yellow	
Pr_6O_{11}	6.91	2183	942.6	892.4	Black	Light green

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TABLE 2

Characteristics of the structure of porcelain	Porcelain paste				
	with no additives (standard)	with 5% Er_2O_3	with 5% Nd_2O_3	with 5% CeO_2	with 5% Pr_6O_{11}
Amount of residual quartz, %	13.7	14.1	12.9	13.6	14.0
Quartz grain size, μm:					
average	17.5	18.2	17.2	20.7	20.1
maximum	120 – 130	120	120	120	120 – 130
Fusion of quartz grains, μm	1 – 2	1 – 2	1 – 2	1 – 2	1 – 3
Porosity, %	7.2	11.0	7.2	9.1	9.6
Pore size, μm:					
average	14.0	14.8	15.0	16.0	16.0
maximum	90 – 100	100 – 120	140	140	100 – 120
Type of porosity	Isolated pores and pores contorted along several pieces	Basically isolated, less frequently contorted	Isolated	Round, less frequently oblong and contorted	Isolated and round
Mullite needle network size, μm	2 – 10 10 – 20	2 – 10 10 – 20	2 – 10 Less frequently 10 – 20	2 – 10 Less frequently 10 – 20	2 – 10 Less frequently 15 – 20
Mullite needle size, μm	1	< 1	< 1	< 1	< 1
Accumulation of mullite	Local	Reticular	Reticular, pronounced	Reticular	Reticular, pronounced
Crystal aggregates, μm	None	10 – 50	None	10 – 130	None

in addition of up to 7% REMO to porcelain paste, and the REMO content subsequently increases undesirably, since the strength decreases sharply.

Rare-earth metal oxides can thus be used for decorating porcelain and the maximum amount in the porcelain paste is 5.0 – 7.5%.

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